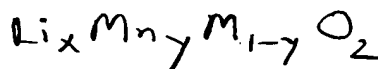


[CLAIMS]

[CLAIM ITEM 1]

A positive pole active substance for non-aqueous electrolytic solution secondary battery is characterized by the fact that shows a monoclinic layer form GANEN [illegible, nalite?] type structure that shown as $\text{Li}_x\text{Mn}_{[illegible y?]} \text{M}_{[illegible 1-y?]} \text{O}_2$ (M shows an element of at the least one type selected from a group comprising Al, Fe, Co, Ni, and Cr; and it is $0 < x \leq 1.1$, $0.5 \leq y < 1$).



[CLAIM ITEM 2]

Manufacturing method of positive pole active substance for non-aqueous electrolytic solution secondary batter in accordance with the claim item 1, wherein manganese compound and compound that includes said element M are hydro thermally treated at $130 \sim 300^\circ\text{C}$ in a strong basic aqueous solution that includes lithium element.

[CLAIM ITEM 3]

The manufacturing method of positive pole active substance for non-aqueous electrolytic solution secondary battery in accordance with the claim item 2, wherein said manganese compound and said compound that includes element M are included in said strong basic aqueous solution after they are co-precipitated and formed as hydroxide, oxide, or oxyhydroxide.

[CLAIM ITEM 4]

The manufacturing method of positive pole active substance for non-aqueous electrolytic solution secondary battery in accordance with the claim item 2, wherein said manganese compound is added to said strong basic aqueous solution after said compound that includes element M is dissolved.

[CLAIM ITEM 5]

The manufacturing method of positive pole active substance for non-aqueous electrolytic solution secondary battery in accordance with the claim items 2,3, or 4, wherein lithium hydroxide is dissolved in said strong basic aqueous solution.

[CLAIM ITEM 6]

The manufacturing method of positive pole active substance for non-aqueous electrolytic solution secondary battery in accordance with the claim items 2,3,4, or 5, wherein potassium hydroxide or sodium hydroxide is dissolved in said strong basic aqueous solution.

[CLAIM ITEM 7]

A non-aqueous electrolytic solution secondary battery is characterized by the fact that has a positive pole of formed body that includes positive active substance for non-aqueous electrolytic solution secondary batter that is described in the claim item 1, a conductive material, and a binder.

(19) 【発行国】 日本国特許庁 (JP)

(12) 【公報種別】 公開特許公報 (A)

(11) 【公開番号】 特開 2000-294242 (P2000-294242A)

(43) 【公開日】 平成 12 年 10 月 20 日 (2000. 10. 20)

(54) 【発明の名称】 非水電解液二次電池用正極活物質、その製造方法及び非水電解液二次電池

(51) 【国際特許分類第 7 版】

H01M 4/58

C01G 45/00

49/00

51/00

53/00

H01M 4/02

10/40

【FI】

H01M 4/58

C01G 45/00

49/00 A

51/00 A

53/00 A

H01M 4/02 C

10/40 Z

【審査請求】 未請求

【請求項の数】 7

【出願形態】 OL

(19) [Publication Office] Japanese Patent Office (JP)

(12) [Kind of Document] Japan Unexamined Patent Publication (A)

(11) [Publication Number of Unexamined Application] Japan Unexamined Patent Publication 2000 - 294242(P2000 - 294242A)

(43) [Publication Date of Unexamined Application] 2000 October 20 day (2000.10.20)

(54) [Title of Invention] ANODE ACTIVE MATERIAL FOR NONAQUEOUS SECONDARY BATTERY, THAT MANUFACTURING METHOD AND NONAQUEOUS ELECTROLYTE SOLUTION SECONDARY BATTERY
(51) [International Patent Classification 7th Edition]

H01M 4/58

C01G 45/00

49/00

51/00

53/00

H01M 4/02

10/40

【FI】

H01M 4/58

C01G 45/00

49/00 A

51/00 A

53/00 A

H01M 4/02 C

10/40 Z

[Request for Examination] Examination not requested

[Number of Claims] 7

[Form of Application] OL

(21) 【出願番号】 特願平 11-102999

(21) [Application Number] Japan Patent Application Hei 11 - 102999

(22) 【出願日】 平成 11 年 4 月 9 日 (1999. 4. 9)

(22) [Application Date] 1999 April 9 day (1999.4.9)

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[Applicant Code] 100 103 584

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【テーマコード (参考)】 4G0024G0485H0035H0145H029

[Theme Code (Reference)] 4G0024G0485H0035H0145H029

【Fターム (参考)】 4G002 AA06 AA10 AB02 AE05 4G048 AA03 AA04 AB02 AC06 AD06 AE05 5H003 AA02 AA04 B A00 BA01 BB05 BB11 BB14 BC01 BD00 BD01 5H014 AA02 BB00 BB01 EE10 HH08 5H029 AJ03 AJ05 AK03 AL06 AL

(57) 【要約】

(57) [Abstract]

【課題】 広い電圧領域で使用でき、容量が大きく、かつ充放電サイクル耐久性に優れた非水電解液二次電池用正極活物質の提供。

[Problem] Be able to use with wide voltage region, offer of an active material for nonaqueous secondary battery to which the capacity is large, at same time is superior in charge-discharge cycle durability.

【解決手段】 単斜晶層状岩塩型構造を有し、 $Li_xMn_yM_{1-y}O_2$ で表される (ただし、Mは、Al、Fe、Co、Ni 及び Cr からなる群から選ばれる 1 種以上の元素

[Means of Solution] (However, M, with element of one kind or more which is chosen from the group which consists of Al, Fe Co, Ni and Cr, is $0 < x \leq 1.1$ and $0.5 \leq y < 1$.) anode active

であり、 $0 < x \leq 1.1$ 、 $0.5 \leq y < 1$ である。) 非水電解液二次電池用正極活物質。

【特許請求の範囲】

【請求項 1】単斜晶層状岩塩型構造を有し、 $\text{Li}_x\text{Mn}_y\text{M}_{1-y}\text{O}_2$ で表される（ただし、Mは、Al、Fe、Co、Ni及びCrからなる群から選ばれる1種以上の元素であり、 $0 < x \leq 1.1$ 、 $0.5 \leq y < 1$ である。）ことを特徴とする非水電解液二次電池用正極活物質。

【請求項 2】リチウム元素を含有する強塩基性水溶液中で、マンガン化合物と前記元素Mを含む化合物とを130～300℃にて水熱処理することを特徴とする請求項1に記載の非水電解液二次電池用正極活物質の製造方法。

【請求項 3】前記マンガン化合物と前記元素Mを含む化合物は、共沈して水酸化物、酸化物又はオキシ水酸化物とされてから前記強塩基性水溶液に含有される請求項2に記載の非水電解液二次電池用正極活物質の製造方法。

【請求項 4】前記強塩基性水溶液には、前記元素Mを含む化合物を溶解させた後、前記マンガン化合物を加える請求項2に記載の非水電解液二次電池用正極活物質の製造方法。

【請求項 5】前記強塩基性水溶液には、水酸化リチウムが溶解している請求項2、3又は4に記載の非水電解液二次電池用正極活物質の製造方法。

【請求項 6】前記強塩基性水溶液には、水酸化カリウム又は水酸化ナトリウムが溶解している請求項2、3、4又は5に記載の非水電解液二次電池用正極活物質の製造方法。

【請求項 7】請求項1に記載の非水電解液二次電池用正極活物質と、導電材と、結合材と、を含む成形体を正極として有することを特徴とする非水電解液二次電池。

【発明の詳細な説明】

material for nonaqueous secondary battery which possesses monoclinic crystal layer halite type structure, is displayed with $\text{Li}_x\text{Mn}_y\text{M}_{1-y}\text{O}_2$.

[Claim(s)]

[Claim 1] It possesses monoclinic crystal layer halite type structure, is displayed with $\text{Li}_x\text{Mn}_y\text{M}_{1-y}\text{O}_2$ (However, M, with element of one kind or more which is chosen from the group which consists of Al, Fe, Co, Ni and Cr, is $0 < x \leq 1.1$ and $0.5 \leq y < 1$.) anode active material for nonaqueous secondary battery which densely is made feature.

[Claim 2] Manufacturing method of anode active material for nonaqueous secondary battery which is stated in Claim 1 which in strong basicity aqueous solution which contains lithium element, hydrothermal treatment does compound which includes the manganese compound and aforementioned element M with 130 to 300 °C and densely makes feature.

[Claim 3] After as for aforementioned manganese compound and compound which includes the aforementioned element M, coprecipitation doing, as hydroxide, oxide or theoxy hydroxide manufacturing method of anode active material for nonaqueous secondary battery which it states in Claim 2 which is contained in aforementioned strong basicity aqueous solution.

[Claim 4] In aforementioned strong basicity aqueous solution, compound which includes the aforementioned element M after melting, manufacturing method of anode active material for nonaqueous secondary battery which is stated in Claim 2 which adds aforementioned manganese compound.

[Claim 5] In aforementioned strong basicity aqueous solution, manufacturing method of anode active material for nonaqueous secondary battery which is stated in the Claim 2 and 3 or 4 which lithium hydroxide is dissolving.

[Claim 6] In aforementioned strong basicity aqueous solution, manufacturing method of anode active material for nonaqueous secondary battery which is stated in the Claim 2, 3, 4 or 5 which potassium hydroxide or sodium hydroxide is dissolving.

[Claim 7] Nonaqueous electrolyte solution secondary battery which anode active material for nonaqueous secondary battery and conductor and binder which are stated in Claim 1 and, possesses molded article which is included densely makes feature as positive electrode and.

[Description of the Invention]

[0001]

【発明の属する技術分野】本発明は、非水電解液二次電池用正極活物質及びその製造方法に関する。さらに該活物質を有する非水電解液二次電池に関する。

[0002]

【従来の技術】近年、機器のポータブル化、コードレス化が進むにつれ、小型、軽量、かつ高エネルギー密度の非水電解液二次電池に対する期待が高まっている。非水電解液二次電池用の正極活物質には、 LiCoO_2 、 LiNiO_2 、 LiMn_2O_4 、 LiMnO_2 等のリチウムと遷移金属との複合酸化物が知られている。これらの正極活物質と、リチウムを吸蔵、放出できる炭素材料等の負極活物質とを組み合わせ、高電圧、高エネルギー密度の非水電解液二次電池の開発が進められている。なかでも特に最近では、安価な材料のマンガンを用いた、リチウムとマンガンの複合酸化物の研究がさかんに進められている。

【0003】一般に、非水電解液二次電池に用いられる正極活物質は、コバルト、ニッケル、マンガン等の遷移金属とリチウムとの複合酸化物からなり、用いられる遷移金属の種類によって電気容量、可逆性、作動電圧等の電極特性が異なる。

【0004】例えば、 LiCoO_2 、及び $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ 等の層状岩塩型構造の複合酸化物を正極活物質に用いた非水電解液二次電池では、容量密度はそれぞれ $140\sim 160\text{mAh/g}$ 及び $190\sim 210\text{mAh/g}$ と比較的高く、 $2.5\sim 4.3\text{V}$ の高い電圧領域ではリチウムの吸蔵、放出に対し良好な可逆性を示す。しかし、原料となるコバルトやニッケルが高価であり、また 2V 以下の電圧領域ではリチウムの吸蔵、放出が可逆的に起こらなくなる問題がある。

【0005】一方、比較的安価なマンガンを原料とする LiMn_2O_4 からなるスピネル型複合酸化物を正極活物質に用いる非水電解液二次電池は、容量密度が $100\sim 120\text{mAh/g}$ であり上述のコバルトやニッケルを含む活物質に比べて低い。また、充放電サイクル耐久性が低く、さらに 3V 未満の低い電圧領域で急速に劣化する問題がある。これに対し、同じくマンガンを原料とする LiMnO_2 を活物質に用いる非水電解液二次電池は、 2

[0001]

[Technological Field of Invention] This invention regards anode active material for nonaqueous secondary battery and its manufacturing method. Furthermore it regards nonaqueous electrolyte solution secondary battery which possesses said active substance.

[0002]

[Prior Art] As recently, portability trend of equipment, cordless trend advances, miniature and the light weight, expectation at same time for nonaqueous electrolyte solution secondary battery of high energy density has increased. Composite oxide of LiCoO_2 , LiNiO_2 , LiMn_2O_4 , LiMnO_2 or other lithium and transition metal is known in positive electrode active material for nonaqueous electrolyte solution secondary battery. Carbon material or other negative electrode active material which intercalation and deintercalation it is possible these positive electrode active material and lithium was combined, development of nonaqueous electrolyte solution secondary battery of high voltage and high energy density is advanced. Especially recently, manganese of inexpensive material was used even among them, research of composite oxide of lithium and manganese is advanced actively.

[0003] Generally, positive electrode active material which is used for nonaqueous electrolyte solution secondary battery, consists of the composite oxide of cobalt, nickel, manganese or other transition metal and lithium, electrical capacity, the reversibility and operating voltage or other electrode characteristic differ in types of transition metal which is used.

[0004] With nonaqueous electrolyte solution secondary battery which uses composite oxide of for example LiCoO_2 , and the $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ or other layer halite type structure for positive electrode active material, as for capacity density respective 140 to 160mAh/g and the 190 to 210mAh/g it is high relatively, with voltage region where 2.5 to 4.3V is high the satisfactory reversibility is shown vis-a-vis intercalation and deintercalation of lithium. But, cobalt or nickel which becomes starting material being expensive, in addition with voltage region of 2V or less there is a problem where intercalation and deintercalation of the lithium stops happening in reversible.

[0005] On one hand, nonaqueous electrolyte solution secondary battery which uses spinel type composite oxide which consists of the LiMn_2O_4 which designates relatively inexpensive manganese as starting material for positive electrode active material, capacity density being 100 to 120mAh/g , is low in comparison with active substance which includes the above-mentioned cobalt or nickel. In addition, charge-discharge cycle durability is low, furthermore is a problem which deteriorates

V前後の低い電圧領域まで作動できるので LiMn_2O_4 より高い容量が期待できるが、充放電サイクル耐久性が LiMn_2O_4 よりさらに低い問題がある。

【0006】 LiMnO_2 としては、 $\beta\text{-NaMnO}_2$ 型構造の斜方晶 LiMnO_2 と $\alpha\text{-NaMnO}_2$ 型構造である層状岩塩型構造の単斜晶 LiMnO_2 が知られている。斜方晶 LiMnO_2 は、充放電の繰り返しにより徐々にスピネル相に転移するため、充放電サイクル耐久性が著しく低い。

【0007】単斜晶 LiMnO_2 は、通常の固相反応法で合成した $\alpha\text{-NaMnO}_2$ を Li イオンを含む非水溶液中で、 300°C 以下の温度でイオン交換することにより合成される(A. R. Armstrong and P. G. Bruce, NATURE, Vol. 381, P499, 1996)。また、リチウム以外のアルカリ金属の水酸化物を含むリチウム塩水溶液中で、マンガン酸化物を水熱処理することにより合成することも報告されている(特開平11-21128)。しかし、これらの方法で合成された単斜晶 LiMnO_2 を正極活物質とすると、充放電サイクル耐久性は改良されるものの、 LiCoO_2 、 $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ 等を正極活物質に用いた非水電解液二次電池に比べれば充放電サイクル耐久性が劣っており、実用電池への採用が困難であった。

【0008】一方、 LiMnO_2 に Fe 、 Ni 、 Co 、 Cr 又は Al を添加した複合酸化物が特開平10-134812に開示されているが、該複合酸化物はいずれもX線回折のチャートがJCPDSの35-749と類似していることから斜方晶 LiMnO_2 構造であると認められ、充放電サイクル耐久性は不十分である。

【0009】

【発明が解決しようとする課題】そこで本発明は、広い電圧領域で使用でき、電気容量が大きく、充放電サイクル耐久性に優れていて、かつ安価な非水電解液二次電池用正極活物質、及びその製造方法を提供することを目的とする。さらに、この正極活物質を用いた高エネルギー密度の非水電解液二次電池を提供することを目的とする。

quickly with voltage region whose under 0.5V is low. Vis-a-vis this, because it can operate nonaqueous electrolyte solution secondary battery which uses LiMnO_2 which similarly designate manganese as starting material for active substance, to the voltage region where approximately 2V is low you can expect the capacity which is higher than LiMn_2O_4 , but charge-discharge cycle durability than LiMn_2O_4 furthermore is lower is a problem which.

[0006] As LiMnO_2 , monoclinic crystal LiMnO_2 of layer halite type construction which is a orthorhombic crystal LiMnO_2 and $\alpha\text{-NaMnO}_2$ type construction of $\beta\text{-NaMnO}_2$ type construction is known. As for orthorhombic crystal LiMnO_2 , in order rearrangement to do gradually in spinel phase with the repetition of charge-discharge, charge-discharge cycle durability is low considerably.

[0007] Monoclinic crystal LiMnO_2 - NaMnO_2 which is synthesized with conventional solid phase reaction method in nonaqueous solution which includes Li ion, is synthesized by ion exchange doing with the temperature of 300°C or below (A. R. Armstrong and P. G. Bruce, NATURE, Vol. 381, P499, 1996). In addition, in lithium salt aqueous solution which includes hydroxide of alkali metal other than lithium, hydrothermal treatment doing by that it synthesizes manganese oxide, it is reported (Japan Unexamined Patent Publication Hei 11-21128). But, when monoclinic crystal LiMnO_2 which is synthesized with these method is designated as positive electrode active material, although if it is improved, you compared the charge-discharge cycle durability to nonaqueous electrolyte solution secondary battery which uses LiCoO_2 and $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ etc for the positive electrode active material, charge-discharge cycle durability was inferior, adoption to practical battery was difficult.

[0008] On one hand, composite oxide which adds Fe, Ni, Co the Cr or Al in LiMnO_2 is disclosed in Japan Unexamined Patent Publication Hei 10-134812, but the said composite oxide is recognized in each case when it is a orthorhombic crystal LiMnO_2 construction from fact that the chart of X-ray diffraction resembles 35-749 of JCPDS, charge-discharge cycle durability is the unsatisfactory.

[0009]

[Problems to be Solved by the Invention] Be able to use this invention, with wide voltage region, electrical capacity to be large, being superior in charge-discharge cycle durability, at same time it offers inexpensive anode active material for nonaqueous secondary battery, the and its manufacturing method densely it makes objective then. Furthermore, nonaqueous electrolyte

[0010]

【課題を解決するための手段】本発明は、単斜晶層状岩塩型構造を有し、 $\text{Li}_x\text{Mn}_y\text{M}_{1-y}\text{O}_2$ で表される（ただし、Mは、Al、Fe、Co、Ni及びCrからなる群から選ばれる1種以上の元素であり、 $0 < x \leq 1$ 、 $0.5 \leq y < 1$ である。）ことを特徴とする非水電解液二次電池用正極活物質、その製造方法及び該正極活物質を有する非水電解液二次電池を提供する。

【0011】 $\text{Li}_x\text{Mn}_y\text{M}_{1-y}\text{O}_2$ は、結晶構造として斜方晶と単斜晶の2種の構造を取りうるが、本発明では単斜晶の層状岩塩型構造を有している。単斜晶のものを非水電解液二次電池の正極活物質として用いると、充放電サイクル耐久性が優れている。ただし、本発明では $\text{Li}_x\text{Mn}_y\text{M}_{1-y}\text{O}_2$ は単斜晶のみからなるものではなく、多少の斜方晶のものが混在していてもよい。

【0012】本発明では、 $\text{Li}_x\text{Mn}_y\text{M}_{1-y}\text{O}_2$ において $0.5 \leq y < 1$ である。 y が0.5未満であると単斜晶層状岩塩構造を維持できなくなる。好ましくは $0.65 \leq y \leq 0.99$ が採用される。また、MはAl、Fe、Co、Ni及びCrからなる群から選ばれる1種以上の元素であるが、特にAlであると本発明の正極活物質を用いた非水電解液二次電池の電気容量が高くなるので好ましい。

【0013】本発明の製造方法では、上記 $\text{Li}_x\text{Mn}_y\text{M}_{1-y}\text{O}_2$ を得るためにリチウム元素を含有する強塩基性水溶液中で、マンガン化合物（以下、Mn源原料という）と元素Mを含む化合物（以下、M源原料という）とを $130 \sim 300^\circ\text{C}$ にて水熱処理する。上記強塩基性水溶液へのMn源原料及びM源原料の添加方法としては、以下の2とおりの方法が好ましく採用される。1）あらかじめ、Mn源原料とM源原料とを均一に混合してから添加する。2）リチウム元素を含有する強塩基性水溶液にM源原料を溶解し、その水溶液中にMn源原料を加える。

solution secondary battery of high energy density which uses this positive electrode active material is offereddensely makes objective.

[0010]

[Means to Solve the Problems] This invention has monoclinic crystal layer halite type structure, is displayed with $\text{Li}_x\text{Mn}_y\text{M}_{1-y}\text{O}_2$ (However, M, with element of one kind or more which is chosen fromthe group which consists of Al, Fe, Co, Ni and Cr, is $0 < x \leq 1$ and $0.5 \leq y < 1$.) anode active material for nonaqueous secondary battery, themanufacturing method and possesses said positive electrode active material nonaqueous electrolyte solution secondary battery which densely are made featureare offered.

[0011] $\text{Li}_x\text{Mn}_y\text{M}_{1-y}\text{O}_2$ can take construction of 2 kinds of orthorhombic crystal and monoclinic crystalas crystal structure, but with this invention it has possessed layer halite type construction of themonoclinic crystal. When it uses those of monoclinic crystal, as positive electrode active material of nonaqueous electrolyte solution secondary battery charge-discharge cycle durabilityis superior. However, with this invention as for $\text{Li}_x\text{Mn}_y\text{M}_{1-y}\text{O}_2$ it is not something whichconsists of only monoclinic crystal, those of some orthorhombic crystal have been allowedto have existed together

[0012] With this invention, it is a $0.5 \leq y < 1$ in $\text{Li}_x\text{Mn}_y\text{M}_{1-y}\text{O}_2$. When y is under 0.5, it cannot maintain monoclinic crystal layer halite construction andbecomes. preferably 0.65 $y \leq 0.99$ is adopted. In addition, M is element of one kind or more which is chosen fromthe group which consists of Al, Fe, Co, Ni and Cr, but when it is a especially Al, because electrical capacity ofthe nonaqueous electrolyte solution secondary battery which uses positive electrode active material of this invention becomes high it isdesirable.

[0013] With manufacturing method of this invention, in strong basicity aqueous solution which contains lithium element in order to obtain above-mentioned $\text{Li}_x\text{Mn}_y\text{M}_{1-y}\text{O}_2$, manganese compound (Below, Mn source starting material you call) with compound (Below, M source starting material you call) which includes element M hydrothermal treatment is done with 130 to 300°C . As Mn source starting material to above-mentioned strong basicity aqueous solution and addition method of Msource starting material, method of according to 2 below isadopted to be desirable. After 1) beforehand, mixing Mn source starting material and M sourcestarting material to uniform, it adds. 2) M source starting material is melted in strong basicity aqueous solution whichcontains lithium element Mn source starting material is added in aqueous solution.

【0014】1)の方法によれば、得られる正極活物質においてMnとMが均一に分布しやすいの好ましい。特に、Mn源原料及びM源原料とを共沈して得られる水酸化物、酸化物又はオキシ水酸化物としてから上記強塩基性水溶液中に含有させると、MnとMがより均一に分布するので好ましい。また、2)の方法も、M源原料が水溶液中に溶解しているためMn源原料と反応しやすいので、得られる正極活物質にはMnとMが均一に分布する。

【0015】MがAlである場合は2)の方法が好ましく、 NaAlO_2 、 KAlO_2 、 LiAlO_2 等を原料として強塩基性水溶液中に溶解させると均質な $\text{LiMn}_x\text{Al}_{1-x}\text{O}_2$ を合成できるので好ましい。

【0016】また、本発明の製造方法において、強塩基性水溶液中に含有されるリチウム元素は作業性や得られる複合酸化物の結晶の均一性から、水溶性のリチウム化合物を強塩基性水溶液に溶解することで該水溶液中に含有させることが好ましく、リチウム化合物としては特に水酸化リチウムが好ましい。

【0017】本発明における強塩基性水溶液は、pH 1以上であることが好ましい。強塩基性水溶液には、リチウム以外のアルカリ金属の水酸化物が含まれていることが好ましい。得られる正極活物質中に不純物が残存しにくいことから、特に水酸化カリウム又は水酸化ナトリウムが好ましい。水酸化カリウムと水酸化ナトリウムは単独で使用しても、混合して使用してもよい。また、強塩基性水溶液中にはアニオンとして、水酸イオンの他に、塩素イオン、臭素イオン、硝酸イオン、酢酸イオン、シュウ酸イオン等が含まれていてもよい。

【0018】本発明の製造方法において、Mn源原料としては、酸化物(Mn_2O_3 、 MnO 、 MnO_2)、酸化物の水和物、オキシ水酸化物等が挙げられるが、3価のマンガン化合物であることが好ましい。これらのMn源原料は、単独で使用しても、2種以上を混合して使用してもよい。

【0019】本発明の製造方法において、M源原料としては、金属M、水酸化物、酸化物、オキシ水酸化物、塩化物、硝酸塩等が使用される。これらのM源原料は、単独で使用してもよく、2種以上を併用してもよい。

[0014] Mn and M amount fabric are easy to do are desirable in uniform 1) according to method, in positive electrode active material which is acquired. Especially, coprecipitation doing Mn source starting material and M source starting material, as the hydroxide, oxide or oxy hydroxide which are acquired after when it contains in above-mentioned strong basicity aqueous solution, because from Mn and the M amount fabric do in uniform, it is desirable. In addition, because 2) also method, because M source starting material is dissolving in aqueous solution, is easy to react with the Mn source starting material, in positive electrode active material which is acquired Mn and the M amount fabric do in uniform.

[0015] When M is Al, 2) method to be desirable, when it melts in strong basicity aqueous solution, with NaAlO_2 , KAlO_2 and LiAlO_2 etc as starting material because uniform $\text{LiMn}_x\text{Al}_{1-x}\text{O}_2$ can be synthesized, it is desirable.

[0016] In addition, lithium element which is contained in strong basicity aqueous solution in manufacturing method of this invention, workability and from uniformity of crystal of composite oxide which is acquired, by fact that water soluble lithium compound is melted in strong basicity aqueous solution contains in said aqueous solution densely to be desirable as lithium compound the especially lithium hydroxide is desirable.

[0017] Strong basicity aqueous solution in this invention is pH 1 or more, it is desirable densely. hydroxide of alkali metal other than lithium is included in strong basicity aqueous solution, it is desirable densely. from fact that impurity is difficult to remain in the positive electrode active material which is acquired, especially potassium hydroxide or sodium hydroxide is desirable. Using and mixing, it is possible to use potassium hydroxide and sodium hydroxide with the alone. In addition, as anion, chlorine ion, bromine ion, nitrate ion, acetate ion and oxalate ion etc may be included by other than hydroxy ion, in the strong basicity aqueous solution.

[0018] In manufacturing method of this invention, as Mn source starting material, oxide (Such as Mn_2O_3 , MnO and MnO_2), you can list the hydrate and oxy hydroxide etc of oxide, but it is a compound of the manganese of trivalent, it is desirable densely. Using and mixing 2 kinds or more, it is possible to use these Mn source starting material, with the alone

[0019] In manufacturing method of this invention, as M source starting material, metal M, the hydroxide, oxide, oxy hydroxide, chloride and nitrate salt etc are used. It is possible to use these M source starting material, with alone, to jointly use 2 kinds or more is possible.

【0020】本発明の製造方法としては、例えば純水 1 kg あたりに水酸化リチウム、塩化リチウム等のリチウム化合物 0.05～5 モルとリチウム以外のアルカリ金属の水酸化物 5～100 モルとを溶解して強塩基性水溶液を調製する。次いでこの水溶液に Mn 源原料と M 源原料を加え、混合した後、得られた混合物をオートクレープ等の水熱反応装置に設置して、水熱反応させる。水熱反応条件としては、通常 130～300℃の温度で 0.5 時間～14 日間反応させることが好ましく、特に 200～250℃の温度で 1～48 時間反応させることが好ましい。

【0021】本発明の製造方法では、強塩基性水溶液 100 mL に対し、Mn 源原料は通常 0.1～10 g 程度加えることが好ましく、特に 0.5～3 g 加えることが好ましい。また、M 源原料は通常 0.02～5 g 程度加えることが好ましく、特に 0.1～1 g 加えることが好ましい。

【0022】水熱反応終了後、残存する水酸化リチウム、水酸化ナトリウム、水酸化カリウム等の未反応原料を除去するため、反応生成物をエタノールで洗浄し濾過し、乾燥することにより、所望の単斜晶層状岩塩型構造の $\text{Li}_x\text{Mn}_y\text{M}_{1-y}\text{O}_2$ が得られる。

【0023】本発明の非水電解液二次電池の正極は、上記正極活性物質と導電材と結合材とを含む成形体である。結合材としては、ポリフッ化ビニリデン、ポリテトラフルオロエチレン（以下、PTFE という）、ポリアミド、カルボキシメチルセルロース、アクリル樹脂等が好ましい。導電材としては、アセチレンブラック、黒鉛、ケッチェンブラック等のカーボン系導電材が好ましい。上記正極活性物質と導電材と結合材との混合物と該結合材を溶解又は分散できる溶媒とからなるスラリー、又は前記混合物に有機溶媒を加えて混練してなる混練物を、アルミニウム箔、ステンレス箔等の正極集電体に塗布又は担持させて正極を成形することが好ましい。

【0024】本発明の非水電解液二次電池において、電解液の溶媒としては炭酸エステルが好ましい。炭酸エステルは環状、鎖状いずれも使用できる。環状炭酸エステルとしてはプロピレンカーボネート、エチレンカーボネート等が例示される。鎖状炭酸エステルとしてはジメチルカーボネート、ジエチルカーボネート、エチルメチルカーボネート、メチルプロピルカーボネート、メチルイ

[0020] As manufacturing method of this invention, melting hydroxide 5 to 100 mole of alkali metal other than the lithium hydroxide, lithium chloride or other lithium compound 0.05 to 5 mole and lithium in for example pure water per kg, it manufactures the strong basicity aqueous solution. Next after mixing to this aqueous solution including Mn source starting material and M source starting material, installing mixture which is acquired in the autoclave or other hydrothermal reaction equipment, hydrothermal reaction it does. As hydrothermal reaction condition, usually 0.5 hours to 14 day it reacts with temperature of the 130 to 300 °C densely to be desirable, 1 to 48-hour it reacts with temperature of especially 200 to 250 °C densely it is desirable.

[0021] With manufacturing method of this invention, usually 0.1 to 10g extent it adds Mn source starting material vis-a-vis strong basicity aqueous solution 100 ml, it is desirable densely, especially 0.5 to 3g it adds, it is desirable densely. In addition, usually 0.02 to 5g extent it adds M source starting material, it is desirable densely, especially 0.1 to 1g it adds, it is desirable densely.

[0022] After hydrothermal reaction ending, in order to remove lithium hydroxide, sodium hydroxide and the potassium hydroxide or other unreacted starting material which remain, you wash reaction product with ethanol and filter, the $\text{Li}_x\text{Mn}_y\text{M}_{1-y}\text{O}_2$ of desired monoclinic crystal layer halite type construction is acquired by drying.

[0023] Positive electrode of nonaqueous electrolyte solution secondary battery of this invention is above-mentioned positive electrode active material and the molded article which includes conductor and binder. As binder, polyvinylidene fluoride and polytetrafluoroethylene (Below, PTFE you call), polyamide carboxymethyl cellulose and the acrylic resin etc are desirable. As conductor, acetylene black, graphite and Ketjen Black or other carbon conductor are desirable. slurry, in or aforementioned consist of solvent which it can melt or can disperse blend and said binder of the above-mentioned positive electrode active material and conductor and binder, or blend the coating fabric or bearing kneaded substance which becomes including organic solvent kneading, in aluminum foil, and stainless steel foil or other positive electrode collector positive electrode forms densely is desirable.

[0024] Carbonate ester is desirable in nonaqueous electrolyte solution secondary battery of this invention, as solvent of the electrolyte solution. carbonate ester cyclic, can use chain in each case. propylene carbonate and ethylene carbonate etc are illustrated as cyclic carbonate ester. dimethyl carbonate, diethyl carbonate, ethyl methyl carbonate, methylpropyl carbonate and methyl isopropyl carbonate etc are illustrated as

ソプロビルカーボネート等が例示される。本発明では上記炭酸エステルを単独で又は２種以上を混合して使用することが好ましく、また上記炭酸エステルを他の溶媒と混合して使用してもよい。

【００２５】また、負極活物質の材料によっては、鎖状炭酸エステルと環状炭酸エステルの混合物を使用すると、放電特性、サイクル耐久性、充放電効率が改良できる場合がある。溶質としては、 ClO_4^- 、 CF_3SO_3^- 、 BF_4^- 、 PF_6^- 、 AsF_6^- 、 SbF_6^- 、 CF_3CO_2^- 、 $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ 等をアニオンとするリチウム塩を使用することが好ましい。

【００２６】さらに、上記電解液の溶媒にフッ化ビニリデン／ヘキサフルオロプロピレン共重合体（例えばアトケム社製カイナー（商品名））、特開平１０－２９４１３１に開示されたフッ化ビニリデン／パーフルオロ（プロピルビニルエーテル）共重合体を添加し、上記の溶質を加えることによりゲル状のポリマー電解質を作製し、電解液のかわりにポリマー電解質を使用してもよい。

【００２７】上記の電解液又はポリマー電解質には、リチウム塩が０．２～２．０ｍｏｌ／Ｌ含まれていることが好ましい。この範囲を逸脱すると、イオン伝導度が低下し、電気伝導度が低下する。より好ましくは０．５～１．５ｍｏｌ／Ｌである。

【００２８】本発明における負極活物質は、リチウムイオンを吸蔵、放出できる材料である。負極活物質は特に限定されないが、例えばリチウム金属、リチウム合金、炭素材料、周期表１４、１５族の金属を主体とした酸化物、炭化ケイ素、酸化ケイ素、硫化チタン、炭化ホウ素等が挙げられる。炭素材料としては、様々な熱分解条件で有機物を熱分解したものや人造黒鉛、天然黒鉛、土壤黒鉛、膨張黒鉛、鱗片状黒鉛等を使用でき、上記酸化物としては、酸化スズを主体とする化合物が使用できる。また、負極集電体としては銅箔、ニッケル箔等が用いられる。

【００２９】本発明における負極は、負極活物質と結合材とからなることが好ましく、負極活物質と結合材との混合物に有機溶媒を加えてスラリーとし、該スラリーを金属箔集電体に塗布、乾燥、プレスして得ることが好ましい。また、正極と負極の間に介在されるセパレータには、多孔質ポリエチレン、多孔質ポリプロピレンフィルム等が好ましく使用される。また、本発明の非水電解液二次

linear carbonate ester. With this invention mixing alone or two kinds or more, uses above-mentioned carbonate ester densely to be desirable, in addition mixing above-mentioned carbonate ester with other solvent, it is possible to use.

[0025] In addition, with material of negative electrode active material, when mixture of linear carbonate ester and cyclic carbonate ester is used, there are times when it can improve discharge property, the cycle durability and charge-discharge efficiency. As solute, uses lithium salt which designates ClO_4^- , CF_3SO_3^- , BF_4^- , PF_6^- , AsF_6^- , SbF_6^- , CF_3CO_2^- and $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ etc as anion densely is desirable.

[0026] Furthermore, it adds vinylidene fluoride / perfluoro (propyl vinyl ether) copolymer which in solvent of the above-mentioned electrolyte solution is disclosed in vinylidene fluoride / hexafluoropropylene copolymer (for example Atochem supplied Kynar (tradename)) and Japan Unexamined Patent Publication Hei 10 - 2941 31, it produces polymer electrolyte of gel by adding above-mentioned solute, is possible to use polymer electrolyte in place of electrolyte solution.

[0027] lithium salt 0.2 to 2.0 mol/l is included in above-mentioned electrolyte solution or the polymer electrolyte, it is desirable densely. When this range it deviates, ionic conductivity decreases, electrical conductivity decreases. It is a more preferably 0.5 to 1.5 mol/l.

[0028] As for negative electrode active material in this invention, it is a material which intercalation and deintercalation it is possible lithium ion. negative electrode active material especially is not limited. You can list oxide, silicon carbide, silicon oxide, titanium sulfide and boron carbide etc which designate metal of for example lithium metal, lithium alloy, carbon material, the Periodic Table 14 and Group 15 as main component. As carbon material, thermal decomposition are done be able to use thing and the artificial graphite, natural graphite, soil graphite, expanded graphite and flake graphite etc which, the compound which designates tin oxide as main component as above-mentioned oxide, can use organic substance with various thermal decomposition condition. In addition, it can use copper foil and nickel foil etc as negative electrode collector.

[0029] Negative electrode in this invention consists of negative electrode active material and binder, it is desirable densely, it makes slurry in blend of negative electrode active material and the binder including organic solvent, coating fabric, drying and press does said slurry in metal foil current collector and can it is desirable densely. In addition, porous polyethylene and porous polypropylene film etc are desirably used for

電池の形状は特に限定されない。シート状（いわゆるフィルム状）、折り畳み状、巻回型有底円筒形、ボタン形等が用途に応じて選択される。

[0030]

【実施例】以下に実施例により本発明を具体的に説明するが、本発明はこれらに限定されない。

【0031】 [例1] PTFE製有底円筒容器に、水酸化カリウム100gと水酸化リチウム水和物1.6gと純水140gとを仕込み、攪拌し溶解させた後、厚さ100μmのアルミニウム箔0.21gを投入し溶解させた。続いて酸化マンガン(Mn_2O_3)粉末1.4gを添加し、さらに攪拌した。次いで溶液が仕込まれている上記円筒容器をステンレス製オートクレーブ内に収納し、オートクレーブ内を窒素ガスで置換した後、密閉系で225℃で10時間水熱処理した。反応終了後、オートクレーブを冷却してスラリー状の内容物を取り出して濾過し、濾液をエタノールで洗浄して水酸化リチウム、水酸化カリウム等を除去し、乾燥して正極活物質粉末を得た。

【0032】 上記粉末のCuK α 線によるX線回折分析の結果、 $2\theta = 18$ 度、37度、39度、45度、62度、65度、67度に回折ピークが認められ、上記粉末は単斜晶相の層状岩塩型 $LiMnO_2$ 構造を有していることがわかった。また、 $2\theta = 15$ 度に微量の斜方晶相の $LiMnO_2$ 構造に基づく回折ピークが認められた。また、粉末の元素分析により、 $LiMn_{0.75}Al_{0.25}O_2$ であることがわかった。

【0033】 上記の $LiMn_{0.75}Al_{0.25}O_2$ 粉末とアセチレンブラックとPTFE粉末とを80:16:4の重量比で混合し、トルエンを添加しつつ混練してシート状に成形した後、乾燥して厚さ150μmの正極を作製し、正極集電体には厚さ20μmのアルミニウム箔を用いた。セパレータには厚さ25μmの多孔質ポリエチレンを用いた。また、厚さ500μmの金属リチウム箔を負極とし、負極集電体にはニッケル箔を用いた。電解液には、エチレンカーボネートとジエチルカーボネートとの容積比で1:1の混合溶媒に1mol/Lの $LiPF_6$ を溶解した溶液を用いた。

【0034】 アルゴングローブボックス中で、上記正極

separator which lies between positive electrode and negative electrode. In addition, shape of nonaqueous electrolyte solution secondary battery of this invention especially is not limited. sheet (so-called film), folded state, wound type cylinder with bottom and button shape etc it is selected according to application.

[0030]

[Working Example(s)] This invention is explained concretely below with Working Example, but this invention is not limited in these.

[0031] [Example 1] In PTFE bottomed cylindrical container, addition, it agitated potassium hydroxide 100g and lithium hydroxide monohydrate 1.6g and the pure water 140g and after melting, threw aluminum foil 0.21g of thickness 100 μm and melted. Consequently it added manganese oxide (Mn_2O_3) powder 1.4g, furthermore agitated. Next, it stored up above-mentioned cylindrical vessel where solution is inserted inside stainless steel autoclave, after substituting inside autoclave with the nitrogen gas, with closed system 10 hours hydrothermal treatment it did with 225 °C. After reaction termination, cooling autoclave, removing contents of slurry, it filtered, washed filter cake with ethanol and removed lithium hydroxide and the potassium hydroxide, etc dried and acquired positive electrode active material powder.

[0032] With CuK line of above-mentioned powder result of x-ray diffraction analysis, the $2\theta = 18$ degrees, degree of 37, 39 degrees, 45 degrees, 6 second; the degree of 65 and it can recognize diffraction peak in degree of 67, the above-mentioned powder has had layer halite type $LiMnO_2$ construction of monoclinic crystal phase, understood densely. In addition, it could recognize diffraction peak which is based on $LiMnO_2$ construction of orthorhombic crystal phase of trace amount in $2\theta = 15$ degrees. In addition, it is a $LiMn_{0.75}Al_{0.25}O_2$ with elemental analysis of powder, understood densely.

[0033] While mixing above-mentioned $LiMn_{0.75}Al_{0.25}O_2$ powder and acetylene black and PTFE powder with weight ratio of 80:16:4, adding toluene kneading, after forming in sheet, drying, it produced positive electrode of thickness 150 μm, used the aluminum foil of thickness 20 μm to positive electrode collector. porous polyethylene of thickness 25 μm was used to separator. In addition, metallic lithium foil of thickness 500 μm was designated as negative electrode, then nickel foil was used to negative electrode collector. solution which melts $LiPF_6$ of 1 mol/l in mixed solvent of 1:1 with volume ratio of ethylene carbonate and diethyl carbonate was used to electrolyte solution.

[0034] In argon glovebox, through separator, opposing, with el

と上記負極とをセパレータを介して対向させ、電解液とともにステンレス製筒形セルに收容し密閉して非水電解液二次電池を得た。0.2 mA/cm²の定電流で4.3 Vまで充電した後、2.0 Vまで放電して初期放電容量を求めた。さらに0.2 mA/cm²の定電流で充放電サイクルを50回繰り返した。2.0~4.3 Vにおける初期放電容量は160 mAh/gであり、50回充放電サイクル後の容量は152 mAh/gであった。

【0035】【例2】水酸化カリウム100gのかわりに水酸化ナトリウム71gを使用し、アルミニウム箔0.21gのかわりに水酸化アルミニウム0.36gを使用した以外は例1と同様に正極活物質粉末を合成した。例1と同様にX線回折分析を行ったところ、単斜晶の層状岩塩型LiMnO₂構造を有し、また2θ=15度に微量の斜方晶からなるLiMnO₂構造に基づく回折ピークが認められた。また、元素分析によりLiMn_{0.85}Al_{0.15}O₂であることがわかった。

【0036】上記正極活物質を用いた以外は例1と同様にして非水電解液二次電池を作製し、例1と同様に評価したところ、初期放電容量は156 mAh/gであり、50回充放電サイクル後の容量は140 mAh/gであった。

【0037】【例3】容積1LのPTFE製有底円筒容器を用い、硝酸マンガンを硝酸アルミニウムとを3:1のモル比で含む水溶液に水酸化アンモニウム水溶液を加えて共沈させ、150℃で加熱・乾燥して、マンガン-アルミニウム共沈水酸化物（マンガンとアルミニウムの原子比は3:1）10gを得た。

【0038】酸化マンガ粉末とアルミニウム箔のかわりに、上記マンガン-アルミニウム共沈水酸化物粉末1.4gを仕込んだ以外は例1と同様にして合成し、正極活物質粉末を得た。例1と同様にX線回折分析を行ったところ、単斜晶の層状岩塩型LiMnO₂構造を有し、また2θ=15度に微量の斜方晶からなるLiMnO₂構造に基づく回折ピークが認められた。また、元素分析によりLiMn_{0.75}Al_{0.25}O₂であることがわかった。

【0039】上記正極活物質を用いた以外は例1と同様にして非水電解液二次電池を作製し、例1と同様に評価

electrolyte solution itaccommodated above-mentioned positive electrode and above-mentioned negative electrode in stainless steel simple cell and closed airtight and acquired nonaqueous electrolyte solution secondary battery. With constant current of 0.2 mA/cm² to 4.3V after charging, discharging to 2.0V, it sought initial discharge capacity. Furthermore charge-discharge cycle 50 time was repeated with constant current of the 0.2 mA/cm². As for initial discharge capacity in 2.0 to 4.3V with 160 mAh/g, as for capacity after the 50 time charge-discharge cycle it was a 152 mAh/g.

[0035] [Example 2] Sodium hydroxide 71g was used in place of potassium hydroxide 100g, other than using aluminum hydroxide 0.36g in place of aluminum foil 0.21g, positive electrode active material powder was synthesized in same way as the Example 1. When x-ray diffraction analysis was done in same way as Example 1, it possessed the layer halite type LiMnO₂ construction of monoclinic crystal, it could recognize diffraction peak which is based on the LiMnO₂ construction which in addition consists of orthorhombic crystal of trace amount in the 2θ = 15 degrees. In addition, it is a LiMn_{0.85}Al_{0.15}O₂ with elemental analysis, understood densely.

[0036] Other than using above-mentioned positive electrode active material, nonaqueous electrolyte solution secondary battery is produced with as similar to Example 1, when you appraise in same way as the Example 1, as for initial discharge capacity with 156 mAh/g, as for capacity after the 50 time charge-discharge cycle it was a 140 mAh/g.

[0037] [Example 3] Making use of PTFE bottomed cylindrical container of volume 1L, in aqueous solution which includes the manganese nitrate and aluminum nitrate with mole ratio of 3:1 coprecipitation doing including ammonium hydroxide aqueous solution, heating & drying with 150 °C, it acquired manganese-aluminum coprecipitation hydroxide (As for atomic ratio of manganese and aluminum 3:1) 10g.

[0038] Other than inserting above-mentioned manganese-aluminum coprecipitation hydroxide powder 1.4g in place of manganese oxide powder and aluminum foil, it synthesized acquired positive electrode active material powder in same way as the Example 1. When x-ray diffraction analysis was done in same way as Example 1, it possessed the layer halite type LiMnO₂ structure of monoclinic crystal, it could recognize diffraction peak which is based on the LiMnO₂ structure which in addition consists of orthorhombic crystal of trace amount in the 2θ = 15 degrees. In addition, it is a LiMn_{0.75}Al_{0.25}O₂ with elemental analysis, understood densely.

[0039] Other than using above-mentioned positive electrode active material, nonaqueous electrolyte solution secondary battery

したところ、初期放電容量は157mAh/gであり、50回充放電サイクル後の容量は150mAh/gであった。

[0040] [例4] 硝酸アルミニウムのかわりに硝酸コバルトを使用した以外は例3と同様にしてマンガン-コバルト共沈水酸化物（マンガンとコバルトの原子比は3:1）を得て、例3と同様に正極活物質粉末を合成した。例1と同様にX線回折分析を行ったところ、単斜晶の層状岩塩型 LiMnO_2 構造を有し、また $2\theta = 15^\circ$ に微量の斜方晶からなる LiMnO_2 構造に基づく回折ピークが認められた。また、元素分析により $\text{LiMn}_{0.75}\text{Co}_{0.25}\text{O}_2$ であることがわかった。

[0041] 上記正極活物質を用いた以外は例1と同様にして非水電解液二次電池を作製し、例1と同様に評価したところ、初期放電容量は152mAh/gであり、50回充放電サイクル後の容量は135mAh/gであった。

[0042] [例5] 硝酸アルミニウムのかわりに硝酸ニッケルを使用した以外は例3と同様にしてマンガン-ニッケル共沈水酸化物（マンガンとニッケルの原子比は3:1）を得て、例3と同様に正極活物質粉末を合成した。例1と同様にX線回折分析を行ったところ、単斜晶の層状岩塩型 LiMnO_2 構造を有し、また $2\theta = 15^\circ$ に微量の斜方晶からなる LiMnO_2 構造に基づく回折ピークが認められた。また、元素分析により $\text{LiMn}_{0.75}\text{Ni}_{0.25}\text{O}_2$ であることがわかった。

[0043] 上記正極活物質を用いた以外は例1と同様にして非水電解液二次電池を作製し、例1と同様に評価したところ、初期放電容量は158mAh/gであり、50回充放電サイクル後の容量は137mAh/gであった。

[0044] [例6] 硝酸アルミニウムのかわりに硝酸鉄を使用した以外は例3と同様にしてマンガン-鉄共沈水酸化物（マンガンと鉄の原子比は3:1）を得て、例3と同様に正極活物質粉末を合成した。例1と同様にX線回折分析を行ったところ、単斜晶の層状岩塩型 LiMnO_2 構造を有し、また $2\theta = 15^\circ$ に微量の斜方晶からなる LiMnO_2 構造に基づく回折ピークが認められた。また、元素分析により LiMnFeO であるこ

is produced with as similar to Example 1, when you appraise in same way as the Example 1, as for initial discharge capacity with 157 mAh/g, as for capacity after the 50 time charge-discharge cycle it was a 150 mAh/g.

[0040] [Example 4] Other than using cobalt nitrate in place of aluminum nitrate, obtaining manganese - cobalt coprecipitation hydroxide (As for atomic ratio of manganese and cobalt 3:1) with as similar to example 3, it synthesized positive electrode active material powder in same way as example 3. When x-ray diffraction analysis was done in same way as Example 1, it possessed the layer halite type LiMnO_2 structure of monoclinic crystal, it could recognize diffraction peak which is based on the LiMnO_2 structure which in addition consists of orthorhombic crystal of trace amount in the $2\theta = 15^\circ$ degrees. In addition, it is a $\text{LiMn}_{0.75}\text{Co}_{0.25}\text{O}_2$ with elemental analysis, understood densely.

[0041] Other than using above-mentioned positive electrode active material, nonaqueous electrolyte solution secondary battery is produced with as similar to Example 1, when you appraise in same way as the Example 1, as for initial discharge capacity with 152 mAh/g, as for capacity after the 50 time charge-discharge cycle it was a 135 mAh/g.

[0042] [Example 5] Other than using nickel nitrate in place of aluminum nitrate, obtaining manganese - nickel coprecipitation hydroxide (As for atomic ratio of manganese and nickel 3:1) with as similar to example 3, it synthesized positive electrode active material powder in same way as example 3. When x-ray diffraction analysis was done in same way as Example 1, it possessed the layer halite type LiMnO_2 structure of monoclinic crystal, it could recognize diffraction peak which is based on the LiMnO_2 structure which in addition consists of orthorhombic crystal of trace amount in the $2\theta = 15^\circ$ degrees. In addition, it is a $\text{LiMn}_{0.75}\text{Ni}_{0.25}\text{O}_2$ with elemental analysis, understood densely.

[0043] Other than using above-mentioned positive electrode active material, nonaqueous electrolyte solution secondary battery is produced with as similar to Example 1, when you appraise in same way as the Example 1, as for initial discharge capacity with 158 mAh/g, as for capacity after the 50 time charge-discharge cycle it was a 137 mAh/g.

[0044] [Example 6] Other than using iron nitrate in place of aluminum nitrate, obtaining manganese - iron coprecipitation hydroxide (As for atomic ratio of manganese and iron 3:1) with as similar to example 3, it synthesized positive electrode active material powder in same way as example 3. When x-ray diffraction analysis was done in same way as Example 1, it possessed the layer halite type LiMnO_2 structure of monoclinic crystal, it could recognize diffraction peak which is based on

【0045】上記正極活物質を用いた以外は例1と同様にして非水電解液二次電池を作製し、例1と同様に評価したところ、初期放電容量は155mAh/gであり、50回充放電サイクル後の容量は130mAh/gであった。

【0046】[例7] 硝酸アルミニウムのかわりに硝酸クロムを使用した以外は例3と同様にしてマンガン・クロム共沈水酸化物（マンガンとクロムの原子比は3:1）を得て、例3と同様に正極活物質粉末を合成した。例1と同様にX線回折分析を行ったところ、単斜晶の層状岩塩型 LiMnO_2 構造を有し、また $2\theta = 15^\circ$ に微量の斜方晶からなる LiMnO_2 構造に基づく回折ピークが認められた。また、元素分析により $\text{LiMn}_{0.75}\text{Cr}_{0.25}\text{O}_2$ であることがわかった。

【0047】上記正極活物質を用いた以外は例1と同様にして非水電解液二次電池を作製し、例1と同様に評価したところ、初期放電容量は157mAh/gであり、50回充放電サイクル後の容量は135mAh/gであった。

【0048】[例8] 硝酸マンガンと硝酸コバルトとのモル比を17:3として混合した以外は例4と同様にしてマンガン・コバルト共沈水酸化物（マンガンとコバルトの原子比は17:3）を得た後、該共沈水酸化物を550°Cで焼成して混合酸化物とし、この混合酸化物を用いて例3と同様にして正極活物質粉末を合成した。例1と同様にX線回折分析を行ったところ、単斜晶の層状岩塩型 LiMnO_2 構造を有し、また $2\theta = 15^\circ$ に微量の斜方晶からなる LiMnO_2 構造に基づく回折ピークが認められた。また、元素分析により $\text{LiMn}_{0.85}\text{Co}_{0.15}\text{O}_2$ であることがわかった。

【0049】上記正極活物質を用いた以外は例1と同様にして非水電解液二次電池を作製し、例1と同様に評価したところ、初期放電容量は159mAh/gであり、

the LiMnO_2 structure which in addition consists of orthorhombic crystal of trace amount in the $2\theta = 15^\circ$ degrees. In addition, it is a $\text{LiMn}_{0.75}\text{Fe}_{0.25}\text{O}_2$ with elemental analysis, understood densely.

[0045] Other than using above-mentioned positive electrode active material, nonaqueous electrolyte solution secondary battery is produced with as similar to Example 1, when you appraise in same way as the Example 1, as for initial discharge capacity with 155 mAh/g, as for capacity after the 50 time charge-discharge cycle it was a 130 mAh/g.

[0046] [Example 7] Other than using chromium nitrate in place of aluminum nitrate, obtaining manganese - chromium coprecipitation hydroxide (As for atomic ratio of manganese and chromium 3:1) with as similar to example 3, it synthesized positive electrode active material powder in same way as example 3. When x-ray diffraction analysis was done in same way as Example 1, it possessed the layer halite type LiMnO_2 structure of monoclinic crystal, it could recognize diffraction peak which is based on the LiMnO_2 structure which in addition consists of orthorhombic crystal of trace amount in the $2\theta = 15^\circ$ degrees. In addition, it is a $\text{LiMn}_{0.75}\text{Cr}_{0.25}\text{O}_2$ with elemental analysis, understood densely.

[0047] Other than using above-mentioned positive electrode active material, nonaqueous electrolyte solution secondary battery is produced with as similar to Example 1, when you appraise in same way as the Example 1, as for initial discharge capacity with 157 mAh/g, as for capacity after the 50 time charge-discharge cycle it was a 135 mAh/g.

[0048] [Example 8] Other than mixing mole ratio of manganese nitrate and cobalt nitrate as 17:3, after acquiring manganese - cobalt coprecipitation hydroxide (As for atomic ratio of manganese and cobalt 17:3) with as similar to example 4, calcining said coprecipitation hydroxide with 550 °C, it made mixed oxide, it synthesized the positive electrode active material powder to similar to example 3 making use of this mixed oxide. When x-ray diffraction analysis was done in same way as Example 1, it possessed the layer halite type LiMnO_2 structure of monoclinic crystal, it could recognize diffraction peak which is based on the LiMnO_2 structure which in addition consists of orthorhombic crystal of trace amount in the $2\theta = 15^\circ$ degrees. In addition, it is a $\text{LiMn}_{0.85}\text{Co}_{0.15}\text{O}_2$ with elemental analysis, understood densely.

[0049] Other than using above-mentioned positive electrode active material, nonaqueous electrolyte solution secondary battery is produced with as similar to Example 1, when you appraise in

50回充放電サイクル後の容量は140mAh/gであった。

【0050】【例9（比較例）】硝酸アルミニウムを添加しなかった以外は例3と同様にして正極活物質粉末を合成した。例1と同様にX線回折分析を行ったところ、単斜晶の層状岩塩型 LiMnO_2 構造を有し、また $2\theta = 15^\circ$ に微量の斜方晶からなる LiMnO_2 構造に基づく回折ピークが認められた。また、元素分析により LiMnO_2 であることがわかった。

【0051】上記正極活物質を用いた以外は例1と同様にして非水電解液二次電池を作製し、例1と同様に評価したところ、初期放電容量は150mAh/gであり、50回充放電サイクル後の容量は90mAh/gであった。

【0052】

【発明の効果】本発明の正極活物質を有する非水電解液二次電池は、広い電圧領域で使用でき、容量が大きく、充放電サイクル耐久性に優れている。また、本発明の正極活物質は、従来より使用されているコバルトやニッケルのかわりに安価なマンガンを用いているため、低コストで得られる。

same way as the Example 1, as for initial discharge capacity with 159mAh/g, as for capacity after the 50 time charge-discharge cycle it was a 140mAh/g.

[0050] [Example 9(Comparative Example)] Besides aluminum nitrate is not added positive electrode active material powder was synthesized with assimilar to example 3. When x-ray diffraction analysis was done in same way as Example 1, it possessed the layer halite type LiMnO_2 construction of monoclinic crystal, it could recognize diffraction peak which is based on the LiMnO_2 construction which in addition consists of orthorhombic crystal of trace amount in the $2\theta = 15^\circ$. In addition, it is a LiMnO_2 with elemental analysis, understood densely.

[0051] Other than using above-mentioned positive electrode active material, nonaqueous electrolyte solution secondary battery is produced with a similar to Example 1, when you appraise in same way as the Example 1, as for initial discharge capacity with 150mAh/g, as for capacity after the 50 time charge-discharge cycle it was a 90mAh/g.

[0052]

[Effects of the Invention] Be able to use nonaqueous electrolyte solution secondary battery which possesses positive electrode active material of this invention, with the wide voltage region, capacity is large, is superior in charge-discharge cycle durability. In addition, positive electrode active material of this invention because inexpensive manganese is used in place of cobalt or nickel which is used from until recently, is acquired with the low cost.